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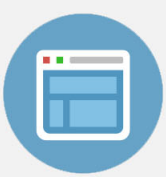

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Anomalous change in dielectric constant of $CaCu_3Ti_4O_{12}$ under violet-to-ultraviolet irradiation

C. Masingboon,[1,2] T. Eknapakul,[1] S. Suwanwong,[1] P. Buaphet,[1] H. Nakajima,[3] S.-K. Mo,[4] P. Thongbai,[5] P. D. C. King,[6,7] S. Maensiri,[1,8,9] and W. Meevasana[1,8,9,a)]
[1]*School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand*
[2]*Faculty of Science and Engineering, Kasetsart University, Chalermphrakiat Sakon Nakhon Province Campus, Sakon Nakhon 47000, Thailand*
[3]*Synchrotron Light Research Institute, Nakhon Ratchasima 30000, Thailand*
[4]*Advanced Light Source, Lawrence Berkeley National Lab, Berkeley, California 94720, USA*
[5]*Department of Physics, Khon Kaen University, Khon Kaen 40000, Thailand*
[6]*SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife KY16 9SS, United Kingdom*
[7]*Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA*
[8]*Thailand Center of Excellence in Physics, CHE, Bangkok 10400, Thailand*
[9]*NANOTEC-SUT Center of Excellence on Advanced Functional Nanomaterials, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand*

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The influence of light illumination on the dielectric constant of $CaCu_3Ti_4O_{12}$ (CCTO) polycrystals is studied in this work. When exposed to 405-nm laser light, a reversible enhancement in the room temperature capacitance as high as 22% was observed, suggesting application of light-sensitive capacitance devices. To uncover the microscopic mechanisms mediating this change, we performed electronic structure measurements, using photoemission spectroscopy, and measured the electrical conductivity of the CCTO samples under different conditions of light exposure and oxygen partial pressure. Together, these results suggest that the large capacitance enhancement is driven by oxygen vacancies induced by the irradiation.
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Ba/Pb-free materials exhibiting large dielectric constants and good thermal stability are widely sought for modern microelectronic and microwave communication systems. A promising compound is perovskite-like $CaCu_3Ti_4O_{12}$ (CCTO), which is not ferroelectric but still exhibits a giant dielectric constant in the kilohertz region ($\sim 10^4$–10^5).[1–3] Moreover, it does not undergo any structural phase transitions over a wide temperature range from −173 to 327 °C, where it maintains its large dielectric constant.[1,2] Several models, such as the internal-barrier-layer-capacitor model[4,5] and the twin or sub-grain model,[6–9] have been employed to explain the giant response in CCTO, and while a full microscopic understanding remains elusive, it is generally thought to be an extrinsic effect related to some form of insulating boundary.[4,5,10–13] The ability to control the electrical property of these insulating boundaries is therefore crucial to modify and enhance the dielectric constant.

Indeed, many studies of poly crystalline samples have already focused on varying the structure of grains and boundaries (for example, by changing calcination temperature,[14] annealing conditions,[15] or additive compounds[16]). Here, we adopt a different approach using light-irradiation of poly crystalline CCTO to dynamically tune its dielectric properties. Such light-irradiation has previously been used to induce a large enhancement in the dielectric constant of $SrTiO_3$ and $KTaO_3$ (Refs. 17 and 18) at temperatures below ~100K, reportedly occurring due to small polaron formation with photo-excited carriers in the quantum paraelectric phase of these compounds.[19] In this work, we observe a striking light-induced enhancement of the dielectric constant in CCTO. This is pronounced even at room temperature, promising applications in light-sensitive electronic devices. We combine spectroscopic and transport measurements performed under different atmospheric conditions to identify the microscopic origin of the capacitance enhancement in this system.

Our CCTO polycrystals were prepared by the solid state reaction method with details described in Ref. 20. CCTO powders were sintered in air at 1050 °C for 6 h. From scanning-electron-microscopy micrographs, the CCTO ceramics were found to have average grain sizes of approximately 2–5 μm in diameter. The dielectric properties were measured using an LCR-meter (Instrek LCR-821). Angle-integrated photoemission spectroscopy (PES) measurements were performed at a temperature of 50 K and base pressure $\sim 7 \times 10^{-11}$ millibar at Beamline 10.0.1, Advanced Light Source, USA. The CCTO polycrystal samples were fractured under vacuum, and the photon beam, which acts as both probe and irradiation source, was set to 60 eV. For the measurements of electrical resistance, electrodes were prepared at BL 6, Synchrotron Light Research Institute (SLRI), Thailand. Then, the measurements were performed under UV light irradiation, using synchrotron light *in situ* at room temperature, and a base pressure of 5×10^{-8} millibar (SLRI BL 3.2 a); the synchrotron light was in zeroth order (i.e., all frequencies with the peak intensity at 60 eV were transmitted through the monochromator).

a)Author to whom correspondence should be addressed. Electronic mail: worawat@g.sut.ac.th

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We fabricated a capacitor with a central CCTO dielectric and a copper back electrode. The front electrode was made of transparent and conductive indium tin oxide (ITO) which was mechanically compressed against the CCTO layer (see the diagram in Fig. 1(f)). The capacitance was then measured using an impedance analyzer outputting an alternating voltage at a frequency (f) of 1 kHz-100 kHz. The CCTO surface was then exposed to violet light from a 405 nm laser through the front (i.e., transparent) electrode. The light intensity was set at 0.2 W/cm^2, and the beam profile was circular with a diameter around 4 mm. This photon energy of 3.06 eV (i.e., 405 nm in wavelength) was chosen to be below the optical band gap of ITO (around 4 eV);[21] hence, most of the light would be transmitted by the top ITO electrode. Additionally, as most materials have work functions above 4 eV, this photon energy of 3.06 eV would not be expected to create photoelectrons, which might artificially affect our measured dielectric constants.

Figs. 1(a)–1(c) show the measured capacitance and loss tangent of the CCTO dielectric. We observed a striking increase of up to 22% in the capacitance measured with f = 1 kHz and 10 kHz under laser light illumination (Figs. 1(a) and 1(b)). In both cases, the capacitance smoothly increased and then saturated after approximately 200 s. When the light was switched off, the capacitance decayed back to the original value with a relatively long time constant of ~2–3 min. This same behavior could be repeated through many cycles of light illumination. We observed a decreasing relative change in the saturated capacitance with frequency, even becoming negative for frequencies of f = 100 kHz, as shown in Fig. 1(d). As shown in Fig. 1(e), the maximum enhancement of the capacitance (shown for f = 1 kHz) shows a dependence on the intensity of the light illumination. Moreover, this suggests that a threshold intensity should be reached before changes in the dielectric constant start to occur, indicative of a chemical change rather than a purely electronic (such as photo-doping) origin of the enhanced capacitance, consistent with our discussions below.

These observations already suggest application of CCTO in light-sensitive tunable capacitance devices. In the

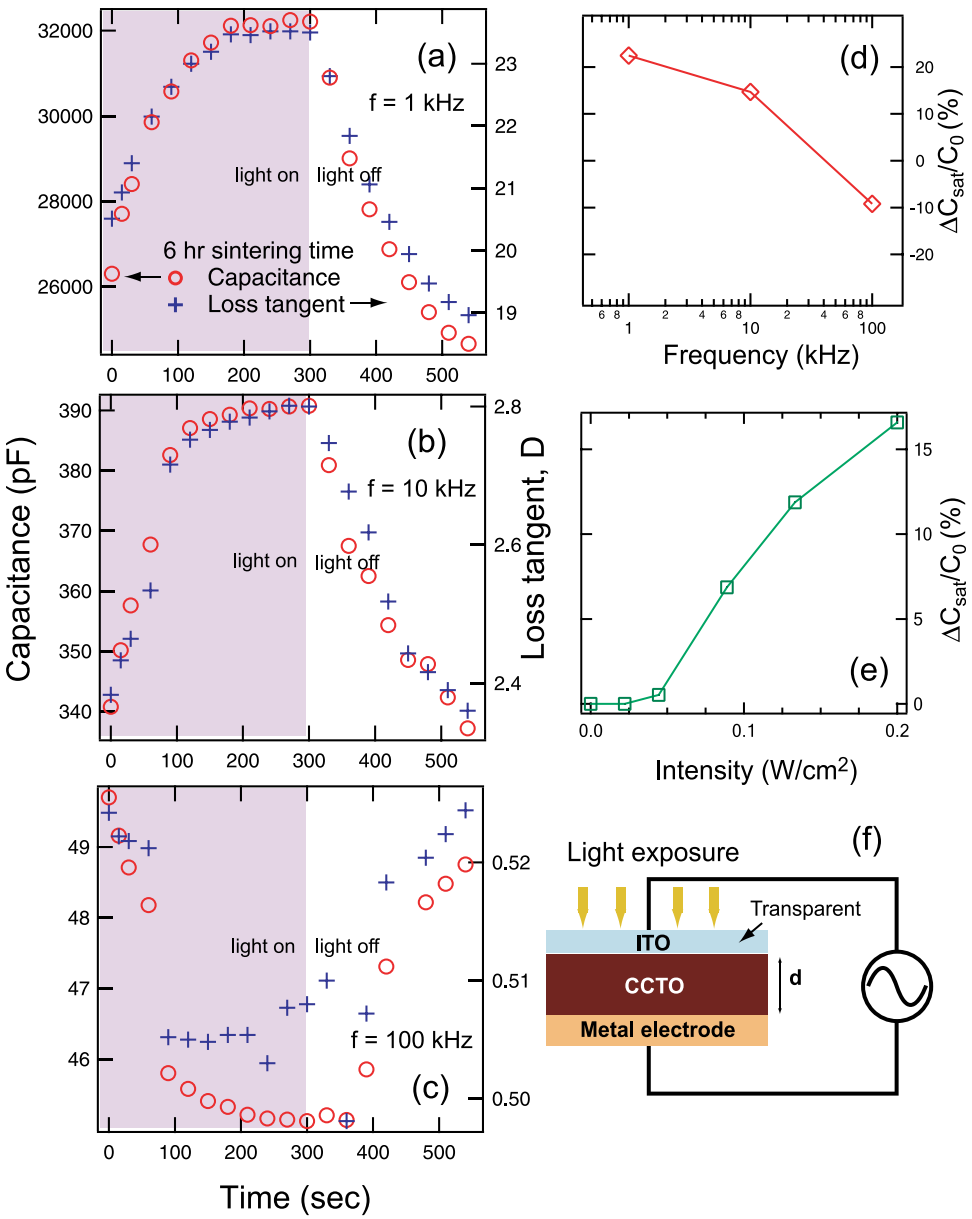

FIG. 1. (a)-(c) Measured capacitance and loss tangent, as a function of light exposure time, of CCTO dielectric materials with sintering time of 6 h. The frequency inputs are 1, 10, and 100 kHz as indicated. (d) The summary of the percentage changes in capacitance at saturation upon the light exposure for all the frequency inputs. (e) The dependence of the capacitance enhancement at 1 kHz (measured on a different sample to the data shown in (a)) as a function of illumination intensity. (f) The diagram of capacitance measurement with CCTO as dielectric material where the light exposure can go through the top transparent gate. All measurements are performed at room temperature.

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following, we attempt to uncover the microscopic mechanism that drives this effect. Firstly, we measured the evolution of the electronic structure of the CCTO samples upon illumination using PES. As shown in Fig. 2(a), the photoemission spectra of the freshly fractured sample shows a valence band characteristic of occupied O_{2p} states at a binding energy of around 4–8 eV. In addition, a small shoulder (marked in Fig. 2(a) as peak B) is observed above the valence band edge, within the band gap. With increased exposure to the intense 60 eV synchrotron light, the PES spectra showed a large depletion of spectral weight from the O_{2p} states (region A), accompanied by an increased weight of the in-gap state (region B). This decrease in relative weight of the A and B peaks with increasing exposure time is shown inset to Fig. 2(a).

For both $SrTiO_3$ (Refs. 22–25) and $KTaO_3$,[26] emergence of a similar in-gap peak has been associated with the creation of oxygen vacancies. In these materials, this mediates the metallicity formation of initially insulating samples.[24,26] To check whether a similar scenario may occur for CCTO, we performed transport measurements in vacuum as a function of UV light exposure. To enable this, we fabricated two silver electrodes with a 1 mm-wide bare surface region in between to be exposed to the incident light (see inset of Fig. 2(b)). At atmospheric pressure, the measured resistance was approximately 160 kΩ. This dropped to 128 kΩ when the sample was held at a pressure of $\approx 5 \times 10^{-8}$ millibar, already suggesting some potential oxygen loss in vacuum. Moreover, as shown in Fig. 2(b), upon UV-light exposure, the resistance showed an initial rapid decrease, followed by a slower decrease with increasing exposure time (corresponding to increased integrated irradiation dose), reaching a decrease of around 2.5% after 1 h. This increase in conductivity agrees well with the development of oxygen-vacancy induced states observed in the photoemission, which should induce metallicity at the sample surface via the chemical reaction O (neutral) $\rightarrow V_0^{++}$ (oxygen vacancy) $+ 2e^- + 1/2\ O_2$.[15] Such oxygen vacancy creation has previously been suggested to occur upon light irradiation in other oxides such as $SrTiO_3$,[24,27] $KTaO_3$,[26] TiO_2, and ZnO.[28] The similarity in the functional form of the resistivity change and the change in relative spectral weight observed in the photoemission (inset of Fig. 2(a)) strongly suggests that this oxygen vacancy creation is occurring here and driving surface metallicity, while the slightly more rapid initial onset in the resistive measurements is consistent with the higher light intensity used than during photoemission.

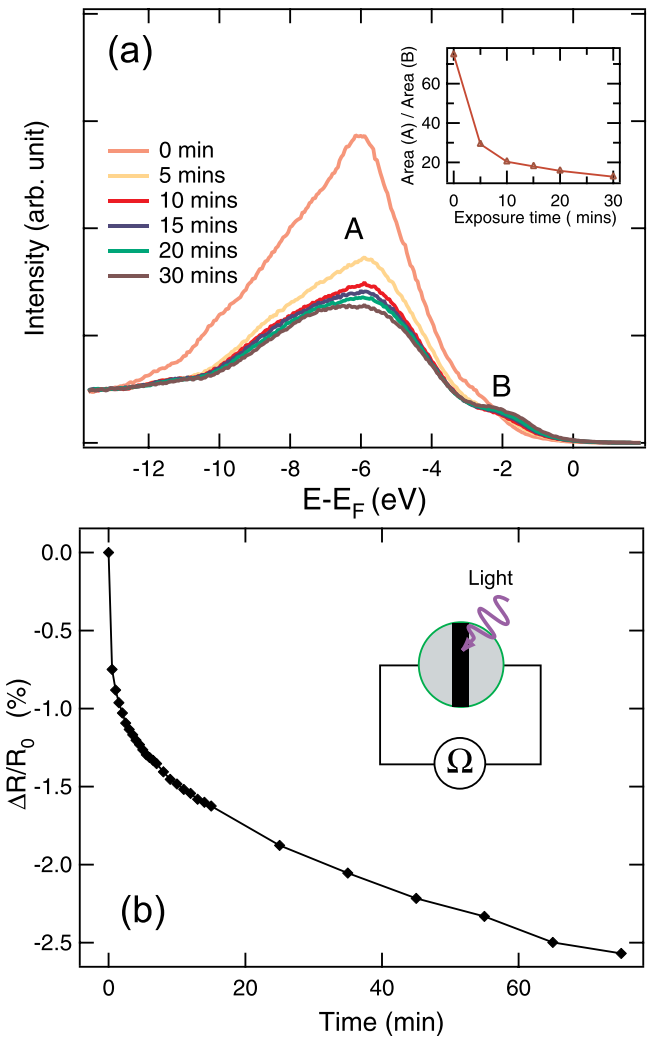

FIG. 2. (a) Evolution of the valance band (VB) spectra of a CCTO ceramic from the pristine fractured surface to the UV-irradiated surface, normalized at high binding energies. Inset shows the ratio between areas of region A and region B as a function of time. (b) The time dependence of the CCTO resistance upon exposure to synchrotron light (zeroth order) at 2.02×10^{-7} millibar ($R_0 = 128.4$ kΩ).

To confirm this hypothesis, we monitored the evolution of the resistance, following light irradiation, while the sample was held in different oxygen partial pressures, as shown in Fig. 3(a). While the reduced resistance induced by light illumination remained fairly stable when the sample was held in vacuum conditions, it showed an increasingly rapid increase with increasing oxygen partial pressure, entirely consistent with the filling of near-surface oxygen vacancies. The similar rate of resistance recovery for the sample held at the highest partial pressure to the rate of decay of the capacitance back to its original value following light illumination (Fig. 1) suggests an intimate link between the oxygen vacancy-induced conductivity in CCTO and the dramatic enhancement of its capacitance. A control experiment using similar pressures of Ar revealed negligible resistance recovery. We note that a similar healing of surface oxygen vacancies by exposure to O_2 gas was also recently demonstrated to reduce surface metallically in In_2O_3.[29]

Such oxygen vacancy creation near the surface following light irradiation (by either our laser, above band gap[30] or absorption edge[31] illumination) provides a plausible explanation for our observation of enhanced capacitance of CCTO. Within the internal-barrier-layer-capacitor (IBLC) model,[4,5] samples consist of semiconducting grains and insulating grain boundaries,[32] and the polarization occurs at these thin boundaries. As these boundaries are much thinner than the total sample thickness, the effective capacitance is enhanced, which leads to a higher value of the averaged dielectric constant for the whole material. As shown schematically in Fig. 3(b), oxygen vacancies induced by irradiation could make some parts of these insulating boundaries become conducting, hence reducing their thickness and enhancing their capacitance. This may be further mediated by oxygen vacancy creation near the sample surface metalizing this region.

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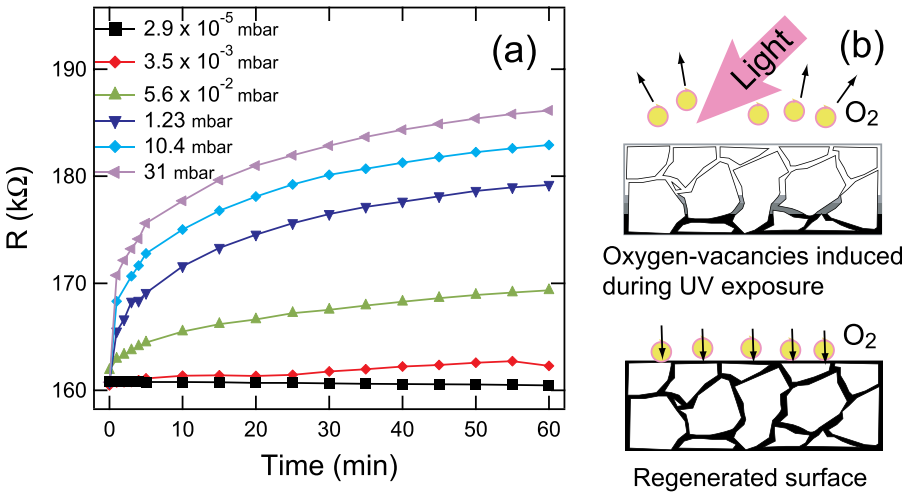

FIG. 3. (a) The time dependence of the CCTO resistance at oxygen pressures between 2.9×10^{-5} and 31 millibar. (b) Schematic diagram of oxygen-vacancy rich surface during UV exposure at low pressure and regenerated surface at high oxygen partial pressure where black and white indicates insulating and conducting regions, respectively.

Healing such vacancies with oxygen exposure would result in a return to the original measured capacitance, consistent with our experiment.

This picture is clearly an oversimplification. CCTO may exhibit a quantum paraelectric effect, as suggested by the data in Refs. 33 and 34. In such a case, the light irradiation could influence the intrinsic dielectric constant as proposed for $SrTiO_3$,[19] in addition to the defect-mediated changes described above. Moreover, neither mechanism naturally accounts for the pronounced dependence of the capacitance enhancement (or even suppression) as a function of frequency (Fig. 1). One possible scenario may relate to the quantum corrections for a narrow confined electron gas if the conducting layer induced by irradiation at the insulating boundaries is thin enough. Recently, Li *et al.* observed a large capacitance enhancement (as high as 40%) for the quantum-confined electron gas at the $SrTiO_3/LaAlO_3$ interface.[35] The confined electrons give rise to the additional quantum capacitance $C_q = Ae^2 \frac{dn}{d\mu}$ which connects in series with the original geometric capacitance. C_q is also frequency dependent and can be either positive or negative, which might explain the contrasting enhancement and suppression seen in our data at frequencies of 1 kHz and 100 kHz, although further detailed theoretical and experimental studies will be required to address this issue.

In summary, we have found pronounced changes in capacitance when a CCTO dielectric material is exposed to intense violet light. Both measurements of electronic structure and conductivity point to a significant role of oxygen vacancies, induced by the light exposure. Moreover, our observations suggest an exciting route for dramatically and reversibly altering the electrical and dielectric properties of CCTO using light exposure, which may be used for in light-sensitive electronic devices.

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[1]A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, Solid State Commun. **115**, 217 (2000).
[2]M. A. Subramanian, L. Dong, N. Duan, B. A. Reisner, and A. W. Sleight, J. Solid State Chem. **151**, 323 (2000).
[3]C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science **293**, 673 (2001).
[4]D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, Appl. Phys. Lett. **80**, 2153 (2002).
[5]T. B. Adams, D. C. Sinclair, and A. R. West, Adv. Mater. **14**, 1321 (2002).
[6]T. T. Fang, L. T. Mei, and H. F. Ho, Acta Mater. **54**, 2867 (2006).
[7]T. T. Fang and H. K. Shiau, J. Am. Ceram. Soc. **87**, 2072 (2004).
[8]S. Krohns, P. Lunkenheimer, S. G. Ebbinghaus, and A. Loidl, Appl. Phys. Lett. **91**, 022910 (2007).
[9]S. F. Shao, J. L. Zhang, P. Zheng, W. L. Zhong, and C. L. Wang, J. Appl. Phys. **99**, 084106 (2006).
[10]P. Lunkenheimer, V. Bobnar, A. V. Pronin, A. I. Ritus, A. A. Volkov, and A. Loidl, Phys. Rev. B **66**, 052105 (2002).
[11]P. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus, and A. Loidl, Phys. Rev. B **70**, 172102 (2004).
[12]L. Zhang and Z. J. Tang, Phys. Rev. B **70**, 174306 (2004).
[13]A. S. West, T. B. Adams, F. D. Morrison, and D. C. Sinclair, J. Eur. Ceram. Soc. **24**, 1439 (2004).
[14]T. Li, R. Xue, J. Hao, Y. Xue, and Z. Chen, J. Alloys Compd. **509**, 1025 (2011).
[15]L. Fang, M. Shen, and W. Cao, J. Appl. Phys. **95**, 6483 (2004).
[16]S. Maensiri, P. Thongbai, and T. Yamwong, Appl. Phys. Lett. **90**, 202908 (2007).
[17]M. Takesada, T. Yagi, M. Itoh, and S. Koshihara, J. Phys. Soc. Jpn. **72**, 37 (2003).
[18]T. Hasegawa, S. Mouri, Y. Yamada, and K. Tanaka, J. Phys. Soc. Jpn. **72**, 41 (2003).
[19]S. Nozawa, T. Iwazumi, and H. Osawa, Phys. Rev. B **72**, 121101 (2005).
[20]P. Thongbai, C. Masingboon, S. Maensiri, T. Yamwong, S. Wongsaenmai, and R. Yimnirun, J. Phys.: Condens. Matter **19**, 236208 (2007).
[21]P. D. C. King, T. D. Veal, F. Fuchs, C. Y. Wang, D. J. Payne, A. Bourlange, H. Zhang, G. R. Bell, V. Cimalla, O. Ambacher, R. G. Egdell, F. Bechstedt, and C. F. McConville, Phys. Rev. B **79**, 205211 (2009).
[22]Y. Aiura, I. Hase, H. Bando, T. Yasue, T. Saitoh, and D. S. Dessau, Surf. Sci. **515**, 61 (2002).
[23]W. Meevasana, X. J. Zhou, B. Moritz, C.-C. Chen, R. H. He, S.-I. Fujimori, D. H. Lu, S.-K. Mo, R. G. Moore, F. Baumberger, T. P. Devereaux, D. van der Marel, N. Nagaosa, J. Zaanen, and Z.-X. Shen, New J. Phys. **12**, 023004 (2010).
[24]W. Meevasana, P. D. C. King, R. H. He, S.-K. Mo, M. Hashimoto, A. Tamai, P. Songsiriritthigul, F. Baumberger, and Z.-X. Shen, Nature Mater. **10**, 114 (2011).
[25]A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhs, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthlmy, and M. J. Rozenberg, Nature (London) **469**, 189 (2011).
[26]P. D. C. King, R. H. He, T. Eknapakul, P. Buaphet, S.-K. Mo, Y. Kaneko, S. Harashima, Y. Hikita, M. S. Bahramy, C. Bell, Z. Hussain, Y. Tokura, Z.-X. Shen, H. Y. Hwang, F. Baumberger, and W. Meevasana, Phys. Rev. Lett. **108**, 117602 (2012).

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[27]S. Mochizuki, F. Fujishiro, and S. Minami, J. Phys.: Condens. Matter **17**, 923 (2005).
[28]J. Liqiang, Q. Yichun, W. Baiqi, L. Shudan, J. Baojiang, Y. Libin, F. Wei, F. Honggang, and S. Jiazhong, Sol. Energy Mater. Sol. Cells **90**, 1773–1787 (2006).
[29]K. H. L. Zhang, R. G. Egdell, F. Offi, S. Iacobucci, L. Petaccia, S. Gorovikov, and P. D. C. King, Phys. Rev. Lett. **110**, 056803 (2013).
[30]L. He, J. B. Neaton, M. H. Cohen, D. Vanderbilt, and C. C. Homes, Phys. Rev. B **65**, 214112 (2002).
[31]J. H. Clark, M. S. Dyer, R. G. Palgrave, C. P. Ireland, J. R. Darwent, J. B. Claridge, and M. J. Rosseinsky, J. Am. Chem. Soc. **133**, 1016 (2011).
[32]S. Y. Chung, I. D. Kim, and S. J. L. Kang, Nature Mater. **3**, 774–778 (2004).
[33]M. Li, A. Feteira, D. C. Sinclair, and A. R. West, Appl. Phys. Lett. **88**, 232903 (2006).
[34]M. Li, A. Feteira, D. C. Sinclair, and A. R. West, Appl. Phys. Lett. **91**, 132911 (2007).
[35]L. Li, C. Richter, S. Paetel, T. Kopp, J. Mannhart, and R. C. Ashoori, Science **332**, 825–828 (2011).

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